

### WHAT WE CLAIM IS:

1. A method of producing an air-entraining cementitious mixture containing fly ash, comprising the steps of:  
forming a cementitious mixture comprising water, cement, fly ash, and an air entrainment agent, and entraining air in the mixture;  
wherein an amount of a sacrificial agent is also included in the cementitious mixture, the sacrificial agent being a material or mixture of materials that, when present in said cementitious mixture in said amount, at least partially neutralizes detrimental effects of components of said fly ash on air entrainment activity of said air entrainment agent, said sacrificial agent present in said amount causing less than 2%vol additional air entrainment in the cementitious mixture.
2. The method of claim 1, wherein said amount of said sacrificial agent exceeds an amount necessary to neutralize said detrimental effects of said components of said fly ash.
3. The method of claim 1, wherein said fly ash may vary in content of said components from a minimum content to a maximum content according to a source or batch of said fly ash, and wherein said amount of said at least one sacrificial agent exceeds an amount necessary to neutralize said detrimental effects of said components of said fly ash when present in said maximum content.
4. The method of claim 1, wherein said sacrificial agent is selected from the group consisting of aromatic compounds bearing either sulfonate, carboxylate or amino functional groups or combinations of said groups, glycols and glycol derivatives having molecular weights of 2000 Da or less, and combinations thereof.
5. The method of claim 1, wherein said sacrificial agent is selected from the group consisting of benzylamine, sodium 1-naphthoate, sodium 2-naphthalene sulfonate, sodium di-isopropyl naphthalene sulfonate, sodium cumene sulfonate, sodium di-butyl naphthalene sulfonate, ethylene glycol phenyl ether, ethylene glycol methyl ether, butoxyethanol, di-ethylene glycol butyl ether, di-propylene glycol methyl ether, polyethylene glycol and 1-phenyl 2-propylene glycol and combinations thereof.

6. The method of claim 1, wherein said sacrificial agent is a member of a class of organic chemicals, said class being selected from the group consisting of alcohols, diols, polyols, ethers, esters, carboxylic acids, carboxylic acid derivatives, aromatic sulfonates, amines, alcoholamines, amides, ammonium salts, and polyglycols.

7. The method of claim 6, wherein said sacrificial agent has a value of  $\text{LogK}_{\text{ow}}$  in the range of -3 to +2.

8. The method of claim 6, wherein said sacrificial agent has a value of  $\text{LogK}_{\text{ow}}$  in the range of -2 to +2.

9. The method of claim 6, wherein said sacrificial agent has an HLB value in the range of -5 to 20.

10. The method of claim 6, wherein said sacrificial agent has an HLB value in the range of -4 to 18.

11. The method of claim 9, wherein said sacrificial agent is a mixture of compounds of different HLB values that together provide the sacrificial agent with an HLB value in said range of -5 to 20.

12. The method of claim 1, wherein said sacrificial agent is an alcohol selected from the group consisting of n-propanol, i-propanol, 1-butanol, 2-butanol, tertiary butanol, 1-pentanol, 3-pentanol, neopentanol, hexanol, benzyl alcohol and phenylethyl alcohol.

13. The method of claim 1, wherein said sacrificial agent is an ether selected from ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol n-propyl ether, ethylene glycol n-butyl ether, ethylene glycol iso-butyl ether, propylene glycol phenyl ether, di-propylene glycol mono methyl ether, di-ethylene glycol butyl ether, ethylene glycol di-methyl ether and p-dimethoxybenzene.

14. The method of claim 1, wherein said sacrificial agent is an ester selected from the group consisting of methyloctanoate, methylaurate, methylpalmitate, methyloleate, ethylene glycol mono-ethyl ether acetate, ethylpropionate, ethylbutyrate, ethylcaproate and POE(20) sorbitan monolaurate.
15. The method of claim 1, wherein said sacrificial agent is a carboxylic acid selected from the group consisting of hexanoic acid, phenyl acetic acid and 2-napthoic acid.
16. The method of claim 1, wherein said sacrificial agent is an aromatic sulfonate selected from the group consisting of 4-ethyl benzene sulfonic acid, 2-naphthalenesulfonate Na, p-toluene sulfonic acid and methyl naphthalene sulfonate.
17. The method of claim 1, wherein said sacrificial agent is an amine selected from the group consisting of triethylamine, n-butyl amine, aniline and benzyl amine.
18. The method of claim 1, wherein said sacrificial agent is an alcoholamine selected from the group consisting of 2-(2-aminoethoxy)ethanol, di-isopropanolamine and tri-isopropanolamine.
19. The method of claim 1, wherein said sacrificial agent is an amide selected from the group consisting of urea, dimethlyurea and n-butyl urea.
20. The method of claim 1, wherein said sacrificial agent is an ammonium salt selected from the group consisting of tetrapropyl ammonium hydroxide and tetrabutyl ammonium chloride.
21. The method of claim 1, wherein said sacrificial agent is a polyglycol selected from the group consisting of tri-ethylene glycol, polyethylene glycol 200, polyethylene glycol 400, polyethylene glycol 2000, tri-propylene glycol, polypropylene glycol 425 and P(EG-ran-propylene-glycol) 2500.

22. The method of claim 1, wherein said sacrificial agent is a compound selected from the group consisting of 2-butanone, methylisobutylketone, butyraldehyde, 1-ethyl-2-pyrrolidinone and n-vinyl-2-pyrrolidinone.

23. The method of claim 1, wherein the sacrificial agent present is a mixture of two or more compounds.

24. The method of claim 1, wherein said sacrificial agent is a compound having hydrophobic lipophilic balance rating in the range of -5 to 20.

25. The method of claim 1, wherein said sacrificial agent is a compound for which LogK<sub>ow</sub> is in the range of -3 to +2.

26. The method of claim 1, wherein said sacrificial agent is a compound for which LogK<sub>ow</sub> is in the range of -2 to +2.

27. The method of claim 1, wherein said sacrificial agent is a compound having a second protocol ranking of 1 or more.

28. The method of claim 1, wherein said sacrificial agent is a compound having a second protocol ranking of 2 or more.

29. The method of claim 1, wherein said sacrificial agent is a compound having a second protocol ranking of 3 or more.

30. The method of claim 1, wherein said sacrificial agent is a compound having a second protocol ranking of 4.

31. The method of claim 1, wherein said sacrificial agent is a combination of ethylene glycol phenyl ether and sodium di-isopropyl naphthalene sulfonate.

32. The method of claim 31, wherein the relative proportion of said ethylene glycol phenyl ether and said sodium di-isopropyl naphthalene sulfonate is in the range of relative weight ratios between 1:5 and 50:1.

33. The method of claim 1, wherein said sacrificial agent is added to said air entrainment agent prior to mixing said air entrainment agent with the fly ash, cement and water.

34. The method of claim 1, wherein said sacrificial agent is added to the fly ash prior to mixing said fly ash with said cement, water and said air entrainment agent.

35. The method of claim 32, wherein said sacrificial agent is added to said fly ash by spraying a liquid containing said sacrificial agent onto said fly ash.

36. The method of claim 32, wherein said sacrificial agent is added to said fly ash by mixing a spray-dried solid containing said sacrificial agent with said fly ash.

37. The method of claim 1, wherein said sacrificial agent is added after the fly ash, cement, water and air entrainment agent have been mixed together.

38. The method of claim 1, wherein said amount of sacrificial agent is at least 0.01% by weight of said fly ash.

39. The method of claim 1, wherein said amount of sacrificial agent is in the range of 0.01 to 2.0% by weight of said fly ash.

40. The method of claim 1, wherein said amount of sacrificial agent is in the range of 0.1 to 1.0% by weight of said fly ash.

41. The method of claim 1, wherein said amount of said sacrificial agents is in the range of 0.01% to 0.5% by weight of the total amount of cementitious material including said fly ash.

42. The method of claim 1, wherein said amount of said sacrificial agents is in the range of 0.01% to 0.2% by weight of the total amount of cementitious material including fly ash.

43. The method of claim 1, wherein an additional material selected from the group consisting of sand, aggregate, and concrete modifier, and a combination thereof, is incorporated into said mixture.

44. An air-entraining cementitious mixture produced by the process of claim 1.

45. A hardened mass of cementitious material produced by setting and hardening the air-entraining cementitious mixture of claim 44.

46. An air-entraining cementitious mixture containing air, water, cement, fly ash, an air entrainment agent and an amount of a sacrificial agent, said sacrificial agent being a material or mixture of materials that, when present in said cementitious mixture in said amount, at least partially neutralizes detrimental effects of components of said fly ash on air entrainment activity of said air entrainment agent, said sacrificial agent present in said amount causing less than 2%vol additional air entrainment in the cementitious mixture.

47. An air-entrained hardened cementitious mass containing air, water, cement, fly ash, an air entrainment agent and an amount of a sacrificial agent, the sacrificial agent being a material or mixture of materials that, when present in a cementitious mixture which is a precursor of said hardened mass, at least partially neutralizes detrimental effects of components of said fly ash on air entrainment activity of said air entrainment agent, said sacrificial agent being used in said cementitious mixture in an amount causing less than 2%vol additional air entrainment in the cementitious mixture.

48. A fly ash composition suitable for use as a component of cementitious mixtures containing an air entrainment agent, said composition comprising fly ash and

a sacrificial agent, the sacrificial agent being a material or mixture of materials that at least partially neutralizes detrimental effects of components of said fly ash on an air entrainment activity of the air entrainment agent upon mixing of said composition with cement, said air entrainment agent and water to form a cementitious mixture, while itself causing less than 2%vol air entrainment in said cementitious mixture.

49. The composition of claim 48, wherein said sacrificial agent is a material or mixture of materials itself causing substantially no air entrainment when used in said mixture.

50. The composition of claim 48, wherein said sacrificial agent is selected from the group consisting of aromatic compounds bearing either sulfonate, carboxylate or amino functional groups or combinations of said groups, glycols and glycol derivatives having molecular weights of 2000 Da or less, and combinations thereof.

51. The composition of claim 48, wherein said sacrificial agent is selected from the group consisting of benzylamine, sodium 1-naphthoate, sodium 2-naphthalene sulfonate, sodium di-isopropyl naphthalene sulfonate, sodium cumene sulfonate, sodium di-butyl naphthalene sulfonate, ethylene glycol phenyl ether, ethylene glycol methyl ether, butoxyethanol, di-ethylene glycol butyl ether, di-propylene glycol methyl ether, polyethylene glycol and 1-phenyl 2-propylene glycol and combinations thereof.

52. The composition of claim 48, wherein said sacrificial agent is a member of a class of organic chemicals, said class being selected from the group consisting of alcohols, diols, polyols, ethers, esters, carboxylic acids, carboxylic acid derivatives, aromatic sulfonates, amines, alcoholamines, amides, ammonium salts, and polyglycols.

53. The composition of claim 52, wherein said sacrificial agent has a value of LogK<sub>ow</sub> in the range of -3 to +2.

54. The composition of claim 52, wherein said sacrificial agent has a value of LogK<sub>ow</sub> in the range of -2 to +2.

55. The composition of claim 52, wherein said sacrificial agent has an HLB value in the range of -5 to 20.

56. The composition of claim 52, wherein said sacrificial agent has an HLB value in the range of -4 to 18.

57. The composition of claim 55, wherein said sacrificial agent is a mixture of compounds of different HLB values that together provide the sacrificial agent with an HLB value in said range of -5 to 20.

58. The composition of claim 48, wherein said sacrificial agent is an alcohol selected from the group consisting of n-propanol, i-propanol, 1-butanol, 2-butanol, tertiary butanol, 1-pentanol, 3-pentanol, neopentanol, hexanol, benzyl alcohol and phenylethyl alcohol.

59. The composition of claim 48, wherein said sacrificial agent is an ether selected from ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol n-propyl ether, ethylene glycol n-butyl ether, ethylene glycol iso-butyl ether, propylene glycol phenyl ether, di-propylene glycol mono methyl ether, di-ethylene glycol butyl ether, ethylene glycol di-methyl ether and p-dimethoxybenzene.

60. The composition of claim 48, wherein said sacrificial agent is an ester selected from the group consisting of methyl octanoate, methyl laurate, methyl palmitate, methyl oleate, ethylene glycol mono-ethyl ether acetate, ethyl propionate, ethyl butyrate, ethyl caproate and POE(20) sorbitan monolaurate.

61. The composition of claim 48, wherein said sacrificial agent is a carboxylic acid selected from the group consisting of hexanoic acid, phenyl acetic acid and 2-naphthoic acid.



62. The composition of claim 48, wherein said sacrificial agent is an aromatic sulfonate selected from the group consisting of 4-ethyl benzene sulfonic acid, 2-naphthalenesulfonate Na, p-toluene sulfonic acid and methyl naphthalene sulfonate.

63. The composition of claim 48, wherein said sacrificial agent is an amine selected from the group consisting of triethylamine, n-butyl amine, aniline and benzyl amine.

64. The composition of claim 48, wherein said sacrificial agent is an alcoholamine selected from the group consisting of 2-(2-aminoethoxy)ethanol, di-isopropanolamine and tri-isopropanolamine.

65. The composition of claim 48, wherein said sacrificial agent is an amide selected from the group consisting of urea, dimethylurea and n-butyl urea.

66. The composition of claim 48, wherein said sacrificial agent is an ammonium salt selected from the group consisting of tetrapropyl ammonium hydroxide and tetrabutyl ammonium chloride.

67. The composition of claim 48, wherein said sacrificial agent is a polyglycol selected from the group consisting of tri-ethylene glycol, polyethylene glycol 200, polyethylene glycol 400, polyethylene glycol 2000, tri-propylene glycol, polypropylene glycol 425 and P(EG-ran-propylene-glycol) 2500.

68. The composition of claim 48, wherein said sacrificial agent is a compound selected from the group consisting of 2-butanone, methylisobutylketone, butyraldehyde, 1-ethyl-2-pyrrolidinone and n-vinyl-2-pyrrolidinone.

69. The composition of claim 48, wherein the sacrificial agent is a mixture of two or more materials.

70. The composition of claim 69, wherein, when used alone as a sacrificial agent in said cementitious mixture, one of said materials reduces air entrainment in

said cementitious mixture and another of said materials increases air entrainment in said cementitious mixture, said materials being used together in relative amounts effective to avoid said sacrificial agent itself increasing or decreasing air entrainment in the cementitious mixture.

71. The composition of claim 48, wherein said sacrificial agent is a material having hydrophobic lipophilic balance rating in the range of -5 to 20.

72. The composition of claim 48, wherein said sacrificial agent is a material for which  $\text{LogK}_{ow}$  is in the range of -3 to +2.

73. The composition of claim 48, wherein said sacrificial agent is a material for which  $\text{LogK}_{ow}$  is in the range of -2 to +2.

74. The composition of claim 48, wherein said sacrificial agent is a compound having a second protocol ranking of 1 or more.

75. The composition of claim 48, wherein said sacrificial agent is a compound having a second protocol ranking of 2 or more.

76. The composition of claim 48, wherein said sacrificial agent is a compound having a second protocol ranking of 3 or more.

77. The composition of claim 48, wherein said sacrificial agent is a compound having a second protocol ranking of 4.

78. The composition of claim 48, wherein said sacrificial agent is a combination of ethylene glycol phenyl ether and sodium di-isopropyl naphthalene sulfonate.

79. The composition of claim 78, wherein the relative proportion of said ethylene glycol phenyl ether and said sodium di-isopropyl naphthalene sulfonate is in the range of relative weight ratios between 1:5 and 50:1.

80. The composition of claim 48, wherein the sacrificial agent is present in said composition at a concentration in an amount of at least 0.01% by weight of said fly ash.

81. The composition of claim 48, wherein the sacrificial agent is present in said composition in an amount in the range of 0.01% to 2% by weight of said fly ash.

82. The composition of claim 48, wherein the sacrificial agent is present in said composition in an amount in the range of 0.01% to 1.0% by weight of fly ash.

83. A method of pre-treating fly ash for use in cementitious mixtures containing an air entrainment agent, comprising mixing an amount of sacrificial agent with fly ash to form a pre-treated fly ash, said sacrificial agent being a material or a mixture of materials that at least partially neutralizes detrimental effects of components of said fly ash on air entrainment activity of an air entrainment agent upon mixing of said pretreated fly ash with cement, said air entrainment agent and water to form a cementitious mixture, while said sacrificial agent itself causing less than 2%vol air entrainment in said cementitious mixture.

84. A mixture of compounds suitable for use as a component of air entraining cementitious mixtures containing fly ash, said mixture of compounds comprising an air entrainment agent and a sacrificial agent, said sacrificial agent being a material or a mixture of materials that at least partially neutralizes detrimental effects of components of fly ash on an air entrainment activity of the air entrainment agent upon mixing of said mixture of materials with cement, fly ash and water to form a cementitious mixture, while said sacrificial agent itself causing less than 2%vol air entrainment in said cementitious mixture.

85. A mixture of compounds suitable for use as a sacrificial agent in the preparation of an air entraining cementitious mixture containing fly ash, said mixture comprising a combination of ethylene glycol phenyl ether and sodium di-isopropyl naphthalene sulfonate.

86. A process of identifying and selecting chemicals as useful sacrificial agents for addition to air entraining fly ash-containing cementitious mixtures that incorporate an air entrainment agent, which process comprises carrying out the following steps in any order on candidate chemicals, and selecting only chemicals identified as suitable according to the following steps:

(a) determining solubility of a candidate chemical in cementitious systems containing different fly ashes having different levels of deleterious components affecting air entrainment, and identifying any partly soluble chemicals;

(b) determining a level of interaction/reaction between a candidate chemical with deleterious components of a fly ash towards air entrainment, and identify chemicals that show partial adsorption onto the fly ash which contain deleterious components towards air entrainment;

(c) evaluating the level of air entrainment by a candidate chemical in portland cement paste and identifying candidates that entrain no air or only low levels of air by themselves;

(d) determining if a candidate chemical shows interference or synergy with typical concrete air entrainment admixtures in portland cement pastes, and identifying candidates that show little or no air entrainment by themselves and little interference on the function and performance of the conventional air entrainment admixture;

(e) determining how effective a candidate chemical may be at reducing variability in air entrainment by a conventional air entrainment agent in fly ash–cement pastes; evaluate paste air entrainment in pastes containing a variety of fly ash having a wide range of properties and residual carbon; identify chemicals that show both increased air entrainment in mixtures and a reduction of 50% or more (relative standard deviation) in the variability of the air entrained in the different fly ash–cement pastes at constant fluidity;

(f) testing and confirming a candidate chemical in fly ash mortars and/or concrete under conditions to identify those having the following features:

(i) enable adequate levels (5-8 vol%) of air to be entrained in concrete or other cementitious products, with dosages of conventional air entrainment agents that are typical of those required when no fly ash, or fly ash with low carbon content (low activity carbon), is used;

(ii) entrain predictable air levels into fly ash-concrete regardless of the variability in the fly ash material, such as the source, carbon content, chemical composition;

(iii) exhibit no interference with cement hydration and concrete set time;

(iv) induce no significant changes to other physical and durability properties of concrete;

(v) are not significantly affected by the presence of other concrete chemical admixtures, for example, water reducers, superplasticizers and set accelerators; and cause no detrimental effects when added in excessive dosages, such as excessive air contents, extended set times, or strength reduction.

87. A process of identifying and selecting chemicals as useful sacrificial agents for addition to air entraining fly ash-containing cementitious compositions that incorporate an air entrainment agent, which process comprises carrying out the following steps on candidate sacrificial agents:

(a) providing a mixture of cement, water and air entrainment agent and measure a volume A of air entrained by said mixture;

(b) providing a mixture of cement, fly ash, water and said air entrainment agent and measure a volume B of air entrained by said mixture, and noting a reduction, volume C, of entrained air between volume A and volume B;

(c) adding said candidate sacrificial agent in an amount to said admixture of cement, fly ash, water and air entrainment agent, and measure a volume of entrained air and note any increase E of entrained air compared with volume B; and

(d) selecting a candidate sacrificial agent for which volume E is at least 50% of volume C.

88. The process of claim 87, wherein said candidate sacrificial agent is added to a mixture of cement, fly ash, water and air entrainment agent in an amount larger than said amount in step (c), and a volume of entrained air is measured and any increase F of entrained air compared with volume B is noted, and wherein a candidate sacrificial agent is selected for which volume F is at least 50% of volume C, even if increase E is less than 50%.

89. The process of claim 87, wherein said amount in step (c) is about 0.05% by weight of said cement and fly ash.

90. The process of claim 88, wherein said larger amount is about 0.1% by weight of said cement and fly ash.

91. The process of claim 87, wherein a candidate sacrificial agent is selected only if said candidate sacrificial agent has a hydrophilic:lipophilic balance in a range of -5 to 20.

92. The process of claim 87, wherein a candidate sacrificial agent is selected only if said candidate sacrificial agent has a hydrophobic:lipophilic balance in a range of -4 to -18.

93. The process of claim 87, wherein a candidate sacrificial agents is selected only if said sacrificial agent has a LogK<sub>ow</sub> value in the range of -3 to +2.

94. The process of claim 87, wherein a candidate sacrificial agents is selected only if said sacrificial agent has a LogK<sub>ow</sub> value in the range of -2 to +2.